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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Insulating Materials

We, RAYCHEM CORPORATION, of Oakside at Northside, Redwood City, California, United States of America, a corporation organized under the laws of the State of California, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an electrical insulating material having improved resistance to heat ageing and to fire, and more especially to a multilayer insulating material.

It is known that polyolefins, for example, polyethylene, may be used in the manufacture of insulating material for electrical conductors and other electrical and electronic components. Such materials suffer from the disadvantage that they have a relatively low melting point, and a low resistance to fire and oxidation, and considerable effort has been directed to the manufacture of compositions having improved properties. It has been proposed, for example, to increase the melting point of polyethylene by cross-linking it, and it has also been proposed to impart the property of flame retardance to polyethylene by combining it with certain additives. Many such additives, however, adversely affect the dielectric properties, corrosion resistance, and the properties at low temperature. Further, the necessity of exposing insulating materials to increasingly severe conditions has increased the standards demanded for the heat and flame resistance, and the strength of polyolefin and other insulating material.

The present invention provides an article for electrical insulation comprising an inner layer comprising a cross-linked olefin polymer and an outer layer comprising a cross-linked homopolymer or copolymer of vinylidene fluoride.

By "inner layer" there is to be understood the layer which, in use, is in contact with, or nearer to, a body to be insulated, while by "outer layer" there is to be understood the layer which, in use, is in contact with, or nearer to, the atmosphere surrounding the body to be insulated.

The present invention further provides an insulated electrical component, advantageously a conductor, preferably a wire, comprising an electrical component at least a portion of which is surrounded by electrical insulation comprising an inner layer comprising a cross-linked olefin polymer and an outer layer comprising a cross-linked vinylidene fluoride homopolymer or copolymer.

The electrical component may be, for example a conducting wire and the invention also provides a method for insulating an electrical conductor which comprises extruding a layer of olefin polymer over an electrical conductor and then extruding a layer of a vinylidene fluoride homopolymer or copolymer over the layer of olefin polymer, both layers being cross-linked.

The olefin polymer may be a polyolefin, for example, polyethylene or polypropylene, or a copolymer of an olefin with any copolymerizable monomer, for example, copolymers of ethylene with butene-1, or vinyl acetate. The polymer may contain a flame retardant for example, an antimony compound, for example, present in an amount equivalent to at least 5% by weight of antimony oxide.

The polymer of vinylidene fluoride is preferably polyvinylidene fluoride, and advantageously contains a minor proportion of triallyl cyanurate, preferably at least 0.5%, of its own weight. The polymer of vinylidene fluoride will hereinafter be referred to for simplicity as polyvinylidene fluoride, but it is to be understood that, unless the context otherwise requires, a copolymer may be used also. The triallyl cyanurate may be incorporated by the processes disclosed in our co-pending applications No. 5501/64 (Specification No. 1047053) and No. 43110/65 (Specification No. 1108990); preferably, the triallyl cyanurate is

present in a proportion of 0.5% to 3% by weight based on the polyvinylidene fluoride. The layers may be cross-linked, for example, by irradiation, for example, by ultra-violet irradiation, irradiation with high energy electrons or by the radiation from an atomic pile, or the polyolefin may be chemically cross-linked, for example, by the incorporation of a free radical initiator, such, for example, as a peroxide when polyethylene is used. When both layers are to be cross-linked by irradiation, they may be irradiated separately or, preferably, simultaneously, in general, both materials are cross-linked through the whole depth of their respective layers.

The degree of cross-linking and other properties of the insulation of the present invention may be varied to suit the application for which the finished material is intended. The inner layer preferably should be cross-linked to an extent equivalent to that provided by irradiation by high energy electrons to a dose of at least 2 megarads, and the polyvinylidene fluoride outer layer should preferably be cross-linked to an extent equivalent to that produced by irradiation polyvinylidene fluoride containing 0.5% by weight of triallyl cyanurate with high energy electrons to a dose of at least 1 megarad. A convenient measure of the cross-linking generally required is that it be sufficient to impart form stability (i.e. the material does not melt or flow but substantially retains its shape) to the composition above its crystallite melting temperature.

For most applications, the thickness of the inner layer will be at least 3 mils, and of the outer layer at least 1.5 mils. Conventional additives may be added to each or either layer to obtain specific desired characteristics.

The insulating material of the present invention possesses a combination of characteristics not found in conventional insulating materials. Particularly surprising is the high degree of flame resistance possessed by the insulating material of the present invention even if no conventional flame retardant systems are added to the highly flammable polyolefin. Although it is to be understood that the present invention is not to be considered to be confined to any particular theory of operation, it would appear possible that the polyvinylidene fluoride outer layer functions to reduce substantially the availability of oxygen to the polyolefin thereby inhibiting flame propagation. The polyvinylidene fluoride itself does not support combustion and when pyrolyzed appears to be converted to a highly stable polynuclear structure. The excellent resistance to heat ageing of the insulating material of the present invention may also be attributed to the function of the polyvinylidene fluoride outer layer of markedly decreasing the availability of oxygen to the polyolefin.

Still another advantage of the present invention is that the polyvinylidene fluoride outer jacket imparts such a high degree of strength that the thickness of insulation may be substantially reduced. This strength in a thin-wall structure complements the light weight and excellent di-electric properties of the polyolefin. The fact that thin-wall structures are made possible by the present invention is of great importance in view of the emphasis on miniaturization of electronic circuitry in modern technology. The same properties make the insulation of the present invention most valuable in applications where light weight is of importance such as in aircraft, missiles and satellites.

The present invention is further illustrated by the following Examples wherein all properties are expressed in parts by weight unless otherwise indicated.

Example 1

A 22 gauge stranded (19/34) tin coated copper conductor having an outside diameter of 0.032 inch was coated with a composition consisting of 81.6 parts high density, high molecular weight polyethylene composition (comprising Tenite 3310R [Tenite is a trade Mark]. 1.1 parts Santonox R, (a sulphide of a dialkyl phenol), 12.9 parts antimony oxide and 2 parts triallyl cyanurate to a thickness of 0.0145 inch thereby giving the insulated wire an outside diameter of 0.061 inch. This insulated wire was then subjected to an irradiation dose of 20 megarads using high energy electrons as the irradiation source. This wire was then coated with a composition consisting of 95.2 parts polyvinylidene fluoride and 2.4 parts triallyl cyanurate. The polyvinylidene fluoride coating imparted a final outside diameter of 0.071 inch to the wire. This wire was then subjected to an irradiation dose of 6 megarads using high energy electrons as the irradiation source.

This wire was then subjected to some standard tests and the results were compared with those obtained for various high temperature insulated wires approved for use by the military, the insulation of which comprised various laminated constructions which are superior to all known polyolefin insulating materials. In the order set forth in Table 1, these insulating materials comprised silicone rubber with an outer dacron-glass braid; polytetrafluoroethylene having an interior layer of mineral powder and polytetrafluoroethylene tape in combination with saturated glass braid.

TABLE 1

Sample (Wire Type)	AWG Size	O.D. (Aver. Inches)	Weight (Aver. lbs./1000 ft.)	Abrasion (Aver. Inches)	Cut-through Dynamic (lbs)	Vertical Flammability Test
MIL—W—8777 (MS 25471)	22	.077	5.18	24.6	120	Fail
MIL—W—22759 (MS 18000)	22	.073	5.61	20.6	23.4	Pass
MIL—W—22759 (MS 90294)	22	.072	5.42	18.5	41.3	Pass
Example 1	22	.071	4.20	24.6	55.3	Pass

The abrasion test was conducted in accordance with MIL—T—5438 using a Janco Abrasion Tester using 4/0 grit garnet paper, a one pound load and one pound tension. The results are expressed in the number of inches of abrasive tape which were required to abrade through the insulation and make contact with the conductor. The dynamic cut through test was conducted by forcing a knife with a 90° edge, 0.005 inch radius, positioned perpendicular to the axis of the wire through the insulation at a rate of 0.2 inch per minute. A potential of 12 volts was maintained between the knife edge and the conductor of the specimen. When the knife edge cut through to the conductor, completion of the 12 volt circuit tripped a relay and recorded the force required to cut through the insulation. The vertical flammability test was conducted according to Federal Specification J—C—98, Method 5221.

Examination of Table 1 clearly shows that the insulation of the present invention had by far the lightest weight, high abrasion and cut through resistance and is capable of passing the flammability test. None of the other insulating materials possesses this combination of properties. The wire designated Ms—25471 was substantially large and possessed good strength characteristics, but burns when subjected to the vertical flammability test. The strength properties of the remaining insulating materials were inferior to those of the insulation of the present invention.

The comparison made in this example was between relatively thick-walled, abrasion resistant insulating materials which are particularly useful for insulating air-frame wire.

EXAMPLE II

A 20 gauge stranded (19/32) tin coated copper conductor having an outside diameter of 0.040 inch was provided with a first coating of polyethylene insulation identical in composition to that described in Example 1 to a thickness of 0.0045 inch to give an outside diameter of 0.049 inch. This insulation was irradiated by high energy electrons to a dose of 20 megarads. This insulated wire was then provided with a second coating consisting of 97% polyvinylidene fluoride and 3% triallyl cyanurate to a thickness of 0.003 inch to give a final

outside diameter of 0.055 inch. This laminated insulation was then irradiated with high energy electrons to a dose of 5 megarads.

The insulating material of this example was then compared with standard thin wall single extrusion insulated wires which are substantially superior to all known polyolefin insulated wires in the same manner as that described in Example 1 and the results of these tests are set forth in Table 2. 400 grit paper with 0.5 pound load and 1.0 pound tension was used for the abrasion test.

TABLE 2

Sample (Wire Type)	AWG Size	O.D. (Aver. Inches)	Weight (Aver. lbs/1000 ft.)	Abrasion (Aver. Inches)	Cut-through Dynamic (lbs.)	Vertical Flammability Test
MIL—W—16878 (Type E — TFE)	20	.059	5.1	25.4	9.3	Pass
MIL—W—16878 (Type B — PVC)	20	.059	4.6	21.4	9.5	Pass
MIL—W—16878 (Type K — FEP)	20	.060	5.2	12.3	6.7	Pass
Example II	20	.055	4.45	28.5	32.9	Pass

Once again, it was observed that although the insulated material of the present invention was substantially lighter than that of the remaining insulating materials, it was superior to them.

EXAMPLE III

In order to determine the effect of the presence of antimony oxide, the composition of the inner layer of an insulating material comprising on outer layer of cross-linked polyvinylidene fluoride and an inner layer of cross-linked polyethylene was varied. Four formulations were prepared, each containing polyethylene (HiFax 1400E), 1.25 parts Santonox R and 2.0 parts triallyl isocyanurate. In addition, formulation 1 contained 91 parts polyethylene and 0 parts antimony oxide; formulation 2 contained 93 parts polyethylene and 5 parts antimony oxide; formulation 3 contained 88 parts polyethylene and 10 parts antimony oxide; and formulation 4 contained 78 parts polyethylene and 20 parts antimony oxide.

Each of these formulations was applied to a conductor in the same manner and size as that set forth in Example II. The polyolefin inner layers were irradiated with high energy electrons to a dose of 10 megarads and a dose of 20 megarads. The outer polyvinylidene fluoride layer was the same for each formulation, had the same composition as that described in Example 1 and was irradiated to a dose of 5 megagrads with high energy electrons. Each sample was subjected to a heat ageing flexibility test (measured in hours at

200°C. until breaking occurred on bending over its own diameter) and to the vertical flammability test of ASTM D 734. The results of the tests are set forth in Table 3.

TABLE 3

Formulation	Polyethylene Dose 10 megarads		Polyethylene Dose 20 megarads	
	Heat ageing (hours)	Vertical flammability (inches)	Heat ageing (hours)	Vertical flammability (inches)
1	113	—	113	7.0
2	121	—	—	6.2
3	121	—	145	4.6
4	—	—	121	4.5

EXAMPLE IV

To establish the necessity of cross-linking both layers of the insulation of the present invention, a series of identical samples was prepared each comprising the same inner polyethylene layer and the same outer polyvinylidene fluoride layer having the same composition and thickness described in Example 1. It was found that when the polyethylene layer was not irradiated, the insulation failed the accelerated ageing test MIL—W—81044/2-(WEP), whether the polyvinylidene fluoride layer was irradiated or not. When these insulated specimens were subjected to the vertical flammability test prescribed by Federal Specification J—C—98, Method 5221, it was found that the specimen in which both layers were irradiated burned for 3.6 inches while the specimen in which the polyethylene layer was irradiated but the polyvinylidene fluoride layer was not irradiated burned 6.5 inches, almost twice as much. A second series of wires having insulation of the same composition and thickness as described in Example II was subjected to the same accelerated ageing test and it was found that only when both layers were irradiated would the insulating material pass this test.

WHAT WE CLAIM IS:—

1. An article for electrical insulation which comprises an inner layer (as hereinbefore defined) comprising a cross-linked olefin polymer and an outer layer comprising a cross-linked homopolymer or copolymer of vinylidene fluoride.

2. An article as claimed in claim 1 wherein the polymer of vinylidene fluoride has been cross-linked by irradiation.

3. An article as claimed in claim 1, wherein the olefin polymer has been cross-linked by irradiation.

4. An article as claimed in claim 1, wherein the olefin polymer and the polymer of vinylidene fluoride have been cross-linked by irradiation.

5. An article as claimed in claim 4, wherein the olefin polymer and the polymer of vinylidene fluoride have been cross-linked simultaneously.

6. An article as claimed in any one of claims 2 to 5 wherein the polymer of vinylidene fluoride comprises at least 0.5% by weight of triallyl cyanurate.

7. An article as claimed in any one of claims 1 to 6, wherein the olefin polymer has been cross-linked to an extent at least equal to that produced by high energy irradiation to a dose of 2 megarads.

8. An article as claimed in any one of claims 1 to 7 wherein the polymer of vinylidene fluoride has been cross-linked to an extent at least equal to that produced in polyvinylidene fluoride containing 0.5% by weight triallyl cyanurate by high energy irradiation to a dose of 1 megarad.

9. An article as claimed in any one of claims 1 to 6, wherein the olefin polymer and the polymer of vinylidene fluoride have each been cross-linked at least to an extent such that, when heated above the respective crystalline melting points, each has form stability.

10. An article as claimed in any one of claims 1 to 9, wherein the olefin polymer is polyethylene.

11. An article as claimed in any one of claims 1 to 10, wherein the olefin polymer contains a flame retardant.

12. An article as claimed in claim 11, wherein the flame retardant is an antimony compound present in a quantity equivalent to at least 5% by weight, based on the weight of the olefin polymer, of antimony oxide.

13. An article as claimed in any one of claims 1 to 12, wherein the polymer of vinylidene fluoride is polyvinylidene fluoride.

14. An article as claimed in claim 1, wherein the polymer of vinylidene fluoride comprises at least 0.5% by weight of triallyl cyanurate.

15. An article as claimed in any one of claims 6 to 14, wherein the polymer of vinylidene fluoride comprises from 0.5% to 3% by weight of triallyl cyanurate.

16. An article as claimed in claim 1, substantially as described in any one of the Examples herein.

17. An insulated electrical component, at least a portion of which is surrounded by insulation which comprises an inner layer comprising a cross-linked olefin polymer and an outer layer comprising a cross-linked homopolymer or copolymer of vinylidene fluoride.

18. An insulated component as claimed in claim 17, which component comprises an electrical conductor.

19. An insulated component as claimed in claim 18, wherein the conductor is a wire.

20. An insulated component as claimed in any one of claims 17 to 19, wherein the insulation comprises a cross-linked olefin polymer and cross-linked polymer of vinylidene fluoride as specified in any one of claims 2 to 13 or 16.

21. An insulated component as claimed in any one of claims 17 to 19, wherein the insulation comprises a cross-linked polymer of vinylidene fluoride as specified in claim 14 or claim 15.

22. A method for insulating an electrical conductor, which comprises extruding a layer of olefin polymer over an electrical conductor, and then extruding a layer of a homopolymer or copolymer of vinylidene fluoride over the layer of olefin polymer, both layers being cross-linked.

23. A method as claimed in claim 22, wherein the polymer of vinylidene fluoride is polyvinylidene fluoride.

24. An article as claimed in any one of claims 1 to 13 wherein each layer has been cross-linked throughout.

25. An article as claimed in claim 14 or claim 15, wherein each layer has been cross-linked throughout.

26. An insulated electrical component as claimed in any one of claims 17 to 20 wherein each layer of the insulation has been cross-linked throughout.

27. An insulated electrical component as claimed in claim 21 wherein each layer of the insulation has been cross-linked throughout.

28. A method as claimed in claim 22 or claim 23, wherein each layer is cross-linked throughout.

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